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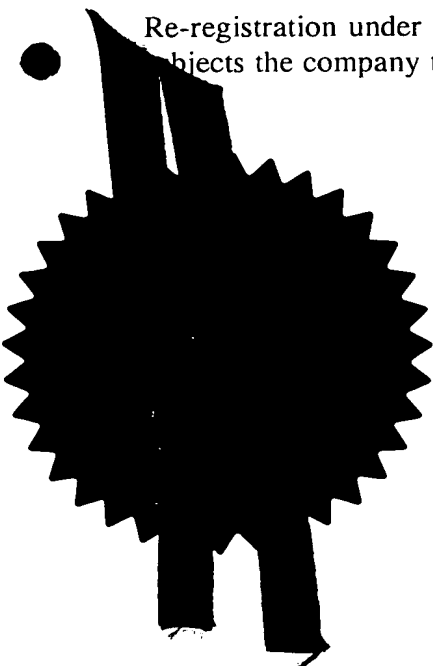
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ELECTROLUMINESCENT DEVICES

This invention relates to electroluminescent devices, especially those that employ an organic material for light emission.

Electroluminescent devices that employ an organic material for light emission are described in PCT/WO90/13148 and US 4,539,507, the contents of both of which are incorporated herein by reference. The basic structure of these devices is a light-emissive organic layer, for instance a film of a poly(p-phenylenevinylene ("PPV")), sandwiched between two electrodes. One of the electrodes (the cathode) injects negative charge carriers (electrons) and the other electrode (the anode) injects positive charge carriers (holes). The electrons and holes combine in the organic layer generating photons. In PCT/WO90/13148 the organic light emissive material is a polymer. In US 4,539,507 the organic light emissive material is of the class known as small molecule materials, such as (8-hydroxyquinolino)aluminium ("Alq"). In a practical device, one of the electrodes is typically transparent, to allow the photons to escape the device.

These devices have great potential for displays. However, there are several significant problems. One is to make the device efficient, particularly as measured by its power efficiency and its external efficiency. Another is to reduce the voltage at which peak efficiency is obtained.

As a preliminary point, it should be noted that the values stated here for energy levels, workfunctions etc. are generally illustrative rather than absolute. The workfunction of ITO can vary widely. Numbers quoted in the literature suggest a range between 4 and 5.2 eV. The 4.8 eV value used here serves as an illustrative rather than an absolute value. The applicant has carried out Kelvin probe measurements which suggest that 4.8 eV is a reasonable value. However, it is well known that the actual value can depend on ITO deposition process and history. For organic semiconductors important characteristics are the binding

energies, measured with respect to the vacuum level of the electronic energy levels, particularly the "highest occupied molecular orbital" ("HOMO") and "lowest unoccupied molecular orbital" ("LUMO") levels. These can be estimated from measurements of photoemission and particularly measurements of the electrochemical potentials for oxidation and reduction. It is well understood in the field that such energies are affected by a number of factors, such as the local environment near an interface, and is the point on the curve (peak) from which the value is determined - e.g. peak, peak base, half-way point - so the use of such values is indicative rather than quantitative.

Figure 1a shows a cross section of a typical device for emitting green light. Figure 1b shows the energy levels across the device. The anode 1 is a layer of transparent indium-tin oxide ("ITO") with a workfunction of 4.8 eV. The cathode 2 is a LiAl layer of with a workfunction of 2.4 eV. Between the electrodes is a light emissive layer 3 of PPV, having a LUMO energy level 5 at around 2.7 eV and a HOMO energy level 6 at around 5.2 eV. Holes and electrons that are injected into the device recombine radiatively in the PPV layer. An important feature of the device is the hole transport layer 4 of polyethylene dioxythiophene ("PEDOT") (see EP 0 686 662 and Bayer AG's Provisional Product Information Sheet for Trial Product AI 4071). This provides an intermediate energy level at 4.8 eV, which helps the holes injected from the ITO to reach the HOMO level in the PPV.

Other organic light emissive materials, having different optical gaps, can take the place of the PPV in order to generate light of other colours. However, at larger optical gaps, towards the blue end of the visible spectrum, the HOMO level is generally well below the corresponding energy level of the ITO. This makes it difficult to inject holes into the emissive layer, i.e. high electric fields are required in order to encourage holes to inject into the semiconductor layer. One solution to this problem would be to choose another material for the anode, but it is difficult to find a preferable alternative because ITO has good transparency, low sheet resistance and established processing routes. Another solution is to add further hole transport layers, so as to provide a series of intermediate energy steps

between the anode and the emissive layer. However, where the layers are deposited from solution it is difficult to avoid one layer being disrupted when the next is deposited, and problems can arise with voids or material trapped between the increased number of inter-layer boundaries.

Considerable advantages can be achieved using a plurality of organic semiconductors within a diode structure; critical to the functioning of such structures is the nature of the interface electronic structure between any two components in contact with one another. A common starting point for such descriptions is that well-known for heterojunctions formed in epitaxially-grown III-V semiconductors. Heterojunctions are classified into classes which include: type I, in which the LUMO and HOMO levels of one material (material A) lie within the LUMO-HOMO energy gap of the second material (material B), as illustrated in figure 2a, and type II, in which the minimum energy difference between the highest HOMO state and the lowest LUMO state is between levels on different sides of the heterojunction, as illustrated in figure 2b. It is generally considered that an electron-hole pair that is in the immediate vicinity of such heterojunctions will arrange so that the electron occupies the lowest LUMO level, and the hole occupies the highest HOMO level. Thus, the electron and hole are present on the same side of the junction for a type I heterojunction, but are separated for the type II heterojunction. An important consequence of this is that electron-hole capture and subsequent light emission is expected for type I but not for type II heterojunctions.

There have been some attempts to combine components in blue-emissive layers. In "Highly Efficient Blue Electroluminescence from a Distyrylarylene Emitting Layer with a new Dopant", Hosokawa et al., Appl. Phys. Lett. 67 (26), 25 December 1995, pp 3853-5 a small molecule device has an emissive layer in which DPVBi is blended with BCzVB or BczVBi. The dopants have a slightly smaller bandgap and a displaced HOMO position compared to the host material. The observed light emission is only from the dopant. This is explained by the authors as arising from Förster energy transfer due to the smaller energy of an

exciton on the dopant molecules. "Efficient Blue-Light Emitting Devices from Conjugated Polymer Blends", Birgerson et al., Adv. Mater 1996, 8, No.12, pp 982-5 describes a blue-light emitting device which employs conjugated polymer blends. The emissive layer of the device consists of a blend of PDHPT with PDPP. These materials form a type I semiconductor interface (see figure 2a), so light emission is from the PDHPT alone. The document emphasises that "it is a necessary but not sufficient requirement that the HOMO-LUMO gap of the light-emitting (guest) polymer be smaller than that of the host polymer. An additional condition is that ... the HOMO energy level of the guest polymer must be at a lower binding energy than that of the host polymer, and the LUMO energy level of the guest polymer must be at a higher binding energy than that of the host polymer".

Two-layer EL devices which exploit the high electron affinity of cyano-derivatives of PPV have shown high efficiencies, as described in US 5,514,878. However, when mixtures are formed with CN-PPV and the soluble PPV, MEH-PPV, as described in "Efficient Photodiodes from Interpenetrating Polymer Networks", J J M Halls et al., Nature, Vol. 376, 10 August 1995, pp498-500 and US 5,670,791, strong quenching of luminescence is observed.

In "Efficient Blue LEDs from a Partially Conjugated Si-Containing PPV Copolymer in a Double-Layer Configuration", Garten et al., Adv. Mater., 1997, 9, No.2, pp127-131 a light emissive device has an emissive layer in which Si-PPV is diluted with PVK to reduce aggregation. The photoluminescent efficiency of the device is observed to increase when aggregation is reduced.

According to a first aspect of the present invention there is provided an electroluminescent device comprising: a first charge carrier injecting layer for injecting positive charge carriers; a second charge carrier injecting layer for injecting negative charge carriers; and a light emissive layer located between the charge carrier injecting layers and comprising a mixture of: a first component for accepting positive charge carriers from the first charge carrier injecting layer; a

second component for accepting negative charge carriers from the second charge carrier injecting layer; and a third, organic light emissive component for accepting and combining charge carriers from the first and second components to generate light.

The process of accepting and combining charge carriers may include acceptance of an exciton from another component and/or acceptance of separate positive and negative charge carriers which subsequently form an exciton.

Preferably one or all of the said components of the light emissive layer is/are phase separated to some extent in the light emissive layer. The light emissive layer suitably comprises regions of each of the said components, which are preferably dispersed through the light emissive layer. Each of those regions suitably comprises substantially only one of the said components, and preferably has the electronic characteristics provided by that component. The components may be evenly or unevenly distributed in the light emissive layer. One or more of the components may be concentrated near the interface of the light emissive layer with the first or second charge carrier injecting layer.

Preferably one or more of the first, second and third components forms a type II semiconductor interface with another of the first, second and third components. A distinction can be made between type II interfaces which do not lead to charge separation (which may be referred to a "luminescent type II interfaces") and those that do lead to charge separation and which, by this or another mechanism, tend to quench luminescence ("non-luminescent type II interfaces"). The type II interfaces referred to herein are suitably of the luminescent type. Luminescent and non-luminescent interfaces can easily be characterised by forming suitable interfaces (as bi-layers or as mixtures formed from solution) and measuring their luminescence behaviour under optical excitation. Methods for measuring the absolute luminescence efficiency are referred to in the paper by Halls et al. cited above.

The applicant considers that it might be possible to understand the underlying principles which govern the behaviour of such type II interfaces by taking into account the role of the binding energy between electron and hole when formed as the neutral excited electronic state (exciton). This "exciton binding energy" is in part due to the electrostatic attraction between electron and hole, and seems to be much stronger in the molecular and polymeric semiconductors which are preferred for use in embodiments of the present invention than in inorganic semiconductors such as III-V materials. The exciton binding energy may act to keep both electron and hole on the same side of a heterojunction. Therefore, in order to achieve charge separation, the energy offsets at the heterojunction as illustrated for the type II case in figure 2b) between HOMO and LUMO (as appropriate) levels may suitably have to be greater than the exciton binding energy.

Most preferably all of the first, second and third components form type II semiconductor interfaces with the others of the first, second and third components. The first component may form a type II semiconductor interface with the second component. The second component may form a type II semiconductor interface with the third component. The first component may form a type II semiconductor interface with the third component. As explained above, all these are suitably "luminescent type II interfaces".

The light emissive layer may comprise other materials, or may consist (or essentially consist) of the first, second and third components.

The third component is preferably a material that is emissive in the visible (e.g. the green or blue) and/or near infrared and/or near ultraviolet regions of the spectrum. The optical gap of the third component is preferably greater than 1.8 eV. When the device is in use there is preferably no (or substantially no) emission from the first and second components. The third component may suitably have an optical gap smaller than the optical gaps of the first and second components. The "optical gap" of a material may be measured as the photon energy at which

the material exhibits strong optical absorption. The third material is preferably a highly efficient luminescent material.

The first component suitably has a LUMO energy level between the LUMO energy levels of the second and third components, suitably to assist the movement of negative charge carriers between the second and third components. The first component suitably has a HOMO energy level between the HOMO energy levels of the second and third components, suitably to assist the movement of positive charge carriers to the second and/or the third components.

The first, second and third components may each be an organic material, suitably a polymer, preferably a conjugated or partially conjugated polymer. Suitable materials include PPV, poly(2-methoxy-5(2'-ethyl)hexyloxyphenylene-vinylene) ("MEH-PPV"), a PPV-derivative (e.g. a di-alkoxy or di-alkyl derivative), a polyfluorene and/or a co-polymer incorporating polyfluorene segments, PPVs and/or related co-polymers. The first and second components (in addition to the third component) may be of light-emissive materials. Alternative materials include organic molecular light-emitting materials, e.g. Alq₃, or any other small sublimed molecule or conjugated polymer electroluminescent material as known in the prior art. The first component may be poly (2,7-(9,9-di-*n*-octylfluorene)-(1,4-phenylene-((4-secbutylphenyl)imino)-1,4-phenylene)) ("TFB"). The second component may be poly (2,7-(9,9-di-*n*-octylfluorene) ("F8"). The third component may be poly(2,7-(9,9-di-*n*-octylfluorene) - (1,4-phenylene-((4-methylphenyl)imino)-1,4-phenylene-((4 - methylphenyl)imino) - 1,4-phenylene)) ("PFM"), poly(2,7 - (9,9 - di-*n*-octylfluorene) - (1,4-phenylene-((4-methoxyphenyl)imino)-1,4-phenylene- ((4-methoxyphenyl)imino)-1,4-phenylene)) ("PFMO") or poly (2,7-(9,9-di-*n*-octylfluorene)-3,6-Benzothiadiazole) ("F8BT"). (See figure 3). Other materials could be used.

The first charge carrier injecting layer may be a positive charge carrier transport layer which is located between the light emissive layer and an anode electrode layer, or may be an anode electrode layer. The second charge carrier injecting

layer may be a negative charge carrier transport layer which is located between the light emissive layer and a cathode electrode layer, or may be a cathode electrode layer.

The anode electrode layer suitably has a workfunction greater than 4.0 eV. The cathode electrode layer suitably has a workfunction less than 3.5 eV.

Either or both of the electrode layers is suitably light transmissive, and preferably transparent, suitably at the frequency of light emission from the device.

According to a second aspect of the present invention there is provided an electroluminescent device comprising: a first charge carrier injecting layer for injecting positive charge carriers; a second charge carrier injecting layer for injecting negative charge carriers; and a light emissive layer located between the charge carrier injecting layers and comprising a mixture of: a first organic light emissive component for accepting and combining positive charge carriers from the first charge carrier injecting layer and negative charge carriers from the second light emissive component to generate light; a second organic light emissive component for accepting and combining negative charge carriers from the second charge carrier injecting layer and positive charge carriers from the first light emissive component to generate light.

Preferably the said components of the light emissive layer are phase separated in the light emissive layer. The light emissive layer suitably comprises regions of each of the said components, which are preferably dispersed through the light emissive layer. Each of those regions suitably comprises substantially only one of the said components, and preferably has the electronic characteristics provided by that component. The components may be evenly or unevenly distributed in the light emissive layer. One of the components may be concentrated near the interface of the light emissive layer with the first or second charge carrier injecting layer.

The first component suitably has a HOMO energy level above that of the second component. The second component suitably has a LUMO energy level above that of the second component. Preferably the first component forms a type II semiconductor interface with the second component.

The light emissive layer may comprise other materials, or may consist (or essentially consist) of the first and second components.

Either or both of the first and second components are preferably materials that is emissive in the visible (e.g. the green or blue) and/or near infrared and/or near ultraviolet regions of the spectrum. The optical gap of either or both of the first and second components is preferably greater than 1.8 eV.

The first and second components may each be an organic material, suitably a polymer, preferably a conjugated or partially conjugated polymer. Suitable materials include PPV, poly(2-methoxy-5(2'-ethyl)hexyloxyphenylene-vinylene) ("MEH-PPV"), a PPV-derivative (e.g. a di-alkoxy or di-alkyl derivative), a polyfluorene and/or a co-polymer incorporating polyfluorene segments, PPVs and/or related co-polymers. Alternative materials include organic molecular light-emitting materials, e.g. Alq₃, or any other small sublimed molecule or conjugated polymer electroluminescent material as known in the prior art. The first component may be F8. The second component may TFB. Other materials could be used.

The first charge carrier injecting layer may be a positive charge carrier transport layer which is located between the light emissive layer and an anode electrode layer, or may be an anode electrode layer. The second charge carrier injecting layer may be a negative charge carrier transport layer which is located between the light emissive layer and a cathode electrode layer, or may be a cathode electrode layer.

The anode electrode layer suitably has a workfunction greater than 4.0 eV. The cathode electrode layer suitably has a workfunction less than 3.0 eV.

Either or both electrode layers are suitably light transmissive, and preferably transparent, suitably at the frequency of light emission from the device.

For both aspects of the present invention it is preferred that the applied voltage at which the device has maximum power efficiency or external efficiency is below 10 V, preferably below 7 V and most preferably below 4 V. For both aspects of the invention it is preferred that the device has a peak power efficiency of greater than 1 lm/W, preferably greater than 2 lm/W and most preferably greater than 6 lm/W. Especially where the device emits red or blue light its efficiency may be lower than this. For both aspects of the invention it is preferred that the device has a peak external efficiency of greater than 2 Cd/A, preferably greater than 5 Cd/A and preferably greater than 7 Cd/A. The above values are especially applicable to devices having green emissions.

For both aspects of the present invention it is preferred that the thickness of the emissive layer is below 400nm, and most preferably in the range from 80 to 160nm.

An aspect important to the present invention, as further developed below, is that the conventional description of heterojunctions does not generally apply for the molecular and polymeric semiconductors which are described here. In particular, although type II heterojunctions are sometimes effective at charge separation (with no light emission), there are important circumstances when they are capable of providing efficient emission of light. As illustrated below, this possibility for the desirable properties of a "type II" heterojunction is not recognised in the prior art. Furthermore, there is no prior art which leads to the realisation of EL diodes which contain type II junctions and which show reduced operating voltages by virtue of the presence of the several semiconductor components present.

The device may suitably have a photoluminescence efficiency greater than 30%.

The present invention will now be described by way of example with reference to the accompanying drawings, in which:

figure 3 shows the chemical structures of some materials discussed below;

figure 4 is a band diagram for an electroluminescent device;

figure 5 is a graph plotting the efficiency of the device of figure 4 against voltage;

figure 6 is a band diagram for a second electroluminescent device;

figure 7 is a graph plotting the efficiency of the device of figure 6 against voltage;

figure 8 shows the emission spectrum of the device of figure 6;

figure 9 is a band diagram for a third electroluminescent device;

figure 10 is a graph plotting the efficiency of the device of figure 9 against voltage;

figure 11 shows the emission spectrum of the device of figure 9;

figure 12 is a band diagram for a fourth electroluminescent device;

figure 13 is a graph plotting the efficiency of the device of figure 12 against voltage;

figure 14 shows the emission spectrum of the device of figure 12;

figure 15 is a band diagram for a fifth electroluminescent device;

figure 16 is a graph plotting the efficiency of the device of figure 15 against voltage;

figure 17 is a graph plotting the efficiency of a sixth electroluminescent device against voltage;

figure 18 is a band diagram for the device of figure 17;

figure 19 is a graph plotting the efficiency of a seventh electroluminescent device against voltage;

figure 20 is a band diagram for an eighth electroluminescent device; and

figure 21 is a band diagram for a ninth electroluminescent device.

Table 1 gives material properties of some light emissive materials:

Table 1

Material	Photoluminescence Efficiency (%)	HOMO Level (eV)	LUMO Level (eV)	Optical gap (eV)	Emission Colour
F8	80	5.8	2.8	3.0	Blue
TFB	40	5.3	2.3	3.0	Blue
PFMO	40	5.0	2.0	3.0	Blue
PFM	20	5.0	2.1	2.9	Blue
5F8BT	95	5.9	3.5	2.4	Green

The photoluminescence efficiencies were measured using the technique of Halls et al. (see above). The HOMO positions were estimated from electrochemical measurement. The optical gaps were determined from the UV/visible absorbance spectrum. The LUMO positions were estimated from the HOMO position and the optical gap. 5F8BT is an abbreviation for a blend of 5% F8BT with 95% F8.

Of the blue emitters, F8 has the highest PL efficiency of these materials. Therefore, of these materials it would normally be the material of choice for a blue emissive layer. Figure 4 is a band diagram for a device in which the emissive layer is F8. A layer of poly(2,7-(9,9-di-*n*-octylfluorene)-(1,4-phenylene-(4-imino(benzoic acid)))-1,4-phenylene-(4-imino(benzoic acid))-1,4-phenylene)) ("BFA") is included as an intermediate hole transport layer. Alternatives for BFA are PEDOT-PSS, polyaniline etc. The hole transport layer also serves to block the passage of electrons to the anode. There is a type II semiconductor interface between the BFA and the F8. Figure 5 shows the power efficiency and the external efficiency of the device against drive voltage. Because of the deep HOMO level (5.8 eV) of the F8 relative to the corresponding energy level in the ITO (4.8 eV) the device needs a high drive voltage and has low power efficiency, even with the intermediate layer of BFA. The power efficiency peaks at about 0.03 lm/W, which is well below what would be acceptable in a practical device. And because the power efficiency is low there is severe heating in the device and its lifetime is short (a matter of minutes). Even during the measurement period for

the data for figure 5 it was found that the device suffered rapid decay from recrystallisation due to heating. This causes a shift in the emission spectrum of the device, with lower energy emissions increasing relative to high energy emissions.

Figure 6 is a band diagram for a second device, in which the emissive layer is 84% F8 mixed with 16% PFM. A layer of BFA is again included as an intermediate hole transport layer. There are type II semiconductor interfaces between the BFA and the F8, the BFA and the PFM, and the PFM and the F8. Figure 7 shows the power efficiency and the external efficiency of the device against drive voltage. Compared to the device of figures 4 and 5 the peak power efficiency of this device is increased (0.33 lm/W compared to 0.03 lm/W), but the voltage at which the power efficiency peaks is not reduced. This suggests that in this device holes are injected into the F8 host polymer (as in the device of figures 4 and 5) and then localised on PFM segments. Figure 8 shows the emission spectrum from the device (line 10) compared to the spectrum of F8 (line 11). Figure 8 indicates that sufficient recombination does occur on the F8 to suggest that holes are injected into the F8 from the hole transport layer of BFA, but shows that most of the recombination of holes and electrons occurs on the PFM rather than the F8. Thus, localised holes form electron-hole pairs with reasonable probability that the electron can be excited to the PFM region. The peak external efficiency of this device (see figure 7) is around 1 Cd/A which is around a factor of 10 better than the device of figures 4 and 5.

Figure 9 is a band diagram for a third device, in which the emissive layer is 84% F8 mixed with 16% TFB. A layer of BFA is again included as an intermediate hole transport layer. There are type II semiconductor interfaces between at least the BFA and the F8, and the TFB and the F8. Figure 10 shows the power efficiency and the external efficiency of the device against drive voltage. Compared to the device of figures 4 and 5 there is a smaller increase in peak external efficiency (to 0.38 Cd/A) and hence a lower peak power efficiency (around 0.15 lm/W). It is believed that the reduction in drive voltage is due to the HOMO level of the TFB

being roughly coincident with the corresponding energy level of the hole transport material (BFA) – this facilitates hole injection into the matrix of the light emissive layer. Figure 11 shows the emission spectrum from the device, which indicates that emission from the device, and therefore radiative recombination within the device, is split roughly equally between the TFB and the F8 polymers.

Figure 12 is a band diagram for a fourth device, in which the emissive layer is 78% F8 mixed with 15% TFB and 7% PFM. A layer of BFA is again included as an intermediate hole transport layer. There are type II semiconductor interfaces between at least the BFA and the F8, the BFA and the PFM, the TFB and the PFM, the TFB and the F8, and the PFM and the F8. Figure 13 shows the power efficiency and the external efficiency of the device against drive voltage. This device shows remarkable improvements in performance. The peak external efficiency is around 2.4 Cd/A and the peak power efficiency is around 1.05 lm/W. Peak power efficiency occurs at only around 6.5 V. Figure 14 shows the emission spectrum from the device, which indicates that all of the emission is from the PFM. The following table compares these results with the figures for the devices of figures 4 to 11.

Table 2

Composition of emissive layer	Peak power efficiency (lm/W)	Voltage at peak power efficiency (V)	Peak external efficiency (Cd/A)	Emitting material
F8	0.03	8.7	0.074	F8
PFM:F8	0.33	9.0	1	PFM + F8
TFB:F8	0.15	7.0	0.37	TFB + F8
TFB:PFM:F8	1.05	6.5	2.4	PFM

The high efficiency of the device of figures 12 to 14 is especially surprising since its emission is from PFM which, as table 1 shows, has by far the lowest PL efficiency of any of the materials used.

It is believed that in the device of figures 12 to 14 the TFB acts to accept holes from the hole transport layer into the polymer matrix of the emissive layer, the holes then being localised on PFM segments. Thus the TFB acts to promote injection of holes into the emissive layer. The LUMO level of the TFB is roughly half way between those of the F8 and the PFM, so it is believed that the TFB LUMO level also provides an intermediate energy step which enhances the rate of transfer of electrons to the PFM when the device is under bias. Also, PFM has a slightly lower optical gap than F8 or TFB, making it energetically favourable for the excitons to form on the PFM regions.

The device of figures 12 to 14 could be adapted by substituting PFMO for the PFM. PFMO has a PL efficiency of 40% (see table 1) and the resulting device has a power efficiency of up to 1.5 lm/W, with emission being from the PFMO. Since PFMO has the same optical gap as F8 and TFB (see table 1) this result suggests that Förster transfer is not the dominant mechanism by which the exciton is confined to the PFMO polymer, although it can be envisaged that it could enhance efficiency. Instead, it is believed that under bias the energy line-up between the hole transport layer and the TFB promotes hole injection into the matrix of the emissive layer. This is followed by transfer to the lower energy HOMO level of the PFMO. However, when TFB is present there is also an energy step in the LUMO levels roughly half way between those of the PFMO and the F8. Thus, when the device is biased the TFB promotes electron transfer on to PFMO polymer segments. In practice there is likely to be a distortion of the energy levels near the polymer interfaces, unlike the simple representation in figure 12.

This explanation is supported by the results of changing the cathode from LiAl to CaAl. CaAl has a higher workfunction than LiAl. If electron transport through the matrix of the emissive layer were via F8, followed by excitation to the PFM or the PFMO then the use of a higher workfunction material should not affect the efficiency, because the workfunction is still close to the LUMO level of F8. However, if electrons were injected from the LiAl cathode and transferred to the PFM predominantly via the TFB then power efficiency would be expected to fall,

because of the higher drive voltage that would be required to overcome the barrier to electron injection between CaAl and TFB. The applicant has observed no difference in performance between devices with LiAl or CaAl cathodes.

Figure 15 is a band diagram for a green emitting device in which the emissive layer is another two-component polymer mixture. In this device the emissive layer is 95% F8 mixed with 5% F8BT. The F8BT dopant forms a type I semiconductor interface with the host F8, but both form type II semiconductor interfaces with the BFA. Figure 16 shows the power efficiency and the external efficiency of the device against drive voltage. The power efficiency is around 2.0 to 2.5 lm/W. Figure 17 shows the power efficiency and the external efficiency against drive voltage for a device similar to that of figures 15 and 16 but in which the emissive layer is a three-component mixture: of first F8 mixed with F8BT in the ratio 19:1, and then that mixture mixed with TFB in the ratio 4:1 (i.e. (F8:F8BT [0.95:0.05]):TFB [0.75:0.25]). Figure 18 is a band diagram for such a device. Figure 19 shows the power efficiency and the external efficiency against drive voltage for a device similar to that of figures 15 and 16 but in which the emissive layer is mixed as (F8:F8BT [0.95:0.05]):TFB[0.5:0.5]. The results for these three devices are summarised in the following table.

Table 3

Amount of TFB in emissive layer (%)	Peak power efficiency (lm/W)	Voltage at peak power efficiency (V)	Peak external efficiency (Cd/A)	Voltage at peak external efficiency (V)
0	2.4	6.8	5.2	Approx. 8.5
25	6	3.8	8	4.5
50	6.7	3.5	7.8	3.8

As the amount of TFB reaches between 50 and 60% the peak efficiency decreases. There is also an increase in external efficiency when TFB is added, principally over the range from 0 to 20% TFB. This is valuable for practical applications.

It is believed that, as with the three-component blue-emissive mixtures described above, the TFB promotes hole injection into the polymer matrix of the emissive layer, allowing exciplexes to form. In the green-emissive devices the exciplexes have a relatively high probability of forming excitons on the F8BT polymer because of the higher internal field and because by doing so they can reduce energy by Förster transfer (F8BT having the narrowest optical gap in the matrix). This leads to an improvement in the external efficiency and the power efficiency.

The efficiency of this device may be further improved by including in the emissive layer one or more other polymers whose HOMO levels are between those of the TFB and the F8 (e.g. around 5.5 eV). This should promote excitation of holes from the TFB to the emissive material, and at higher bias fields promote hole injection into the matrix of the emissive layer itself.

It should be noted that including PFM in the green-emissive blend substantially reduces device efficiency. This is believed to be due to its relatively shallow HOMO level, which acts as a deep hole trap, rather than as an intermediary, and thus inhibits formation of excitons on the F8BT polymer.

Figures 20 and 21 show some other embodiments of the principles discussed above.

In figure 20 the emissive layer is a mixture of F8BT, F8 and PPV. The F8BT:F8 blend is coated over the PPV and acts as an electron transport layer allowing electron transport between the cathode and the conduction band in the PPV. The addition of the F8BT and F8 to the PPV allow the use of a cathode that is more stable than the usual AlLi cathodes, even though it has a higher workfunction. In figure 18 the cathode is Mg, whose workfunction is 3.5 eV. An alternative is Al, whose workfunction is 4.2 eV. A further improvement could be made by including in the blend a third polymer with a LUMO level between those of F8BT (3.4 eV) and F8 (2.8 eV).

In figure 21 the emissive layer is a mixture of poly(paraphenylene) ("PPP"), TFB and F8 with a CaAl cathode. The principles described above in relation to improving hole injection are applied in this device to improve electron injection.

The devices described above can be fabricated in the conventional way, by deposition of the polymer layers from solution on to a commercially-available glass/ITO substrate, followed by evaporative deposition of the cathode. As an example, the fabrication of the device of figures 4 and 5 will be described in detail. First, on to a commercially-available glass/ITO substrate the BFA is deposited by spin-coating from a 0.8% concentration solution with *N,N*-Dimethylformamide ("DMF") as the solvent. The polymer layer is then dried by heating the sample to 80°C under nitrogen gas for 30 minutes. Then the emissive layer is spin-coated from a 1.6% concentration solution with mixed xylene as the solvent. Targets for the thicknesses of the BFA layer and the emissive layer are 10 to 80nm and 60 to 200nm respectively; typical thicknesses are 65nm and 95nm respectively. Finally the cathode is deposited by evaporation to form a 20nm thick layer of Li, followed by a 200nm layer of Al. In an inert atmosphere such as nitrogen the device is encapsulated by sealing within a glass/epoxy encapsulant.

Alternative materials could be used in devices that embody the principles described above. For example, alternative materials for the anode include tin oxide ("TO") and fluorinated TO; alternative materials for the hole transport layer include PEDOT and poly-aniline; alternative materials for the emissive layer include PPV and MEH-PPV; and alternative materials for the cathode include Ca, Yb, Li, Sm and Tb and alloys containing at least one low-workfunction (e.g. LiAl) material. The cathode could be transparent. The hole transport layer could be omitted, or there could be more than one hole transport layer. There could be one or more electron transport layers between the cathode and the emissive layer, which would act to facilitate transfer of electrons from the cathode to the emissive layer and/or to block passage of holes to the cathode.

The hole transport layer could be a mixture of materials. For instance, it could be of BFA blended with a PFM-like polymer but with solution solvency as for the BFA adjusted by the inclusion of carboxylic acid groups. Any electron transport layer could also comprise a mixture of materials, such as F8 and F8BT.

In addition to providing highly efficient blue and green emissive devices, the principles described above could be used for longer wavelength (e.g. red) emissive devices. There are polymers that are highly desirable for such devices because they have deep LUMO levels, which would allow higher workfunction and more stable metals to be used for the cathode, and high PL efficiency. However, those polymers have correspondingly deep HOMO levels. The principles described above would allow those polymers to be used despite their deep HOMO levels.

When fabricating devices with multi-component emissive layers the components can suitably be mixed together before deposition. However, to optimise the electronic effects of the components so as to exploit the principles described above it is preferred that the components in the emissive layer are partially or fully phase-separated, so that within the emissive layer there are dispersed regions of each component (see US 5,760,791, the contents of which are incorporated herein by reference). Where movement of charge carriers from one component to another is desired, the structure of the mixed layer (especially the proportions of these components and the sizes of the regions of each) should preferably provide for adequate interfaces between those components. The regions of each component could be dispersed evenly through the layer or it may be advantageous for one or more of the components to be concentrated near one or other of the interfaces of the light emissive layer with the charge carrier injection layers.

The present invention may include any feature or combination of features disclosed herein either implicitly or explicitly or any generalisation thereof irrespective of whether it relates to the presently claimed invention. In view of the foregoing

description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

CLAIMS

1. An electroluminescent device comprising:
 - a first charge carrier injecting layer for injecting positive charge carriers;
 - a second charge carrier injecting layer for injecting negative charge carriers; and
 - a light emissive layer located between the charge carrier injecting layers and comprising a mixture of:
 - a first component for accepting positive charge carriers from the first charge carrier injecting layer;
 - a second component for accepting negative charge carriers from the second charge carrier injecting layer; and
 - a third, organic light emissive component for accepting and combining charge carriers from the first and second components to generate light.
2. An electroluminescent device as claimed in claim 1, wherein the first component, the second component and the third component are at least partially phase-separated in the light emissive layer.
3. An electroluminescent device as claimed in claim 1 or 2, wherein at least one of the first, second and third components forms a type II semiconductor interface with another of the first, second and third components.
4. An electroluminescent device as claimed in any preceding claim, wherein all of the first, second and third components form type II semiconductor interfaces with the others of the first, second and third components.
5. An electroluminescent device as claimed in any preceding claim, wherein the optical gap of the third component is greater than 1.8 eV.
6. An electroluminescent device as claimed in any preceding claim, wherein the first component is TFB.

7. An electroluminescent device as claimed in any preceding claim, wherein the second component is F8.

8. An electroluminescent device as claimed in any preceding claim, wherein the first component has a LUMO energy level between the LUMO energy levels of the second and third components.

9. An electroluminescent device as claimed in any preceding claim, wherein the third component is PFM.

10. An electroluminescent device as claimed in any of claims 1 to 7, wherein the optical gap of the third component is less than the optical gaps of the first and second components.

11. An electroluminescent device as claimed in any of claims 1 to 7 or 10, wherein the third component is F8BT.

12. An electroluminescent device as claimed in any preceding claim, wherein at least one of the first, second and third components is an organic material.

13. An electroluminescent device as claimed in any preceding claim, wherein at least one of the first, second and third components is a conjugated polymer material.

14. An electroluminescent device as claimed in any preceding claim, wherein the first charge carrier injecting layer is a positive charge carrier transport layer which is located between the light emissive layer and an anode electrode layer.

15. An electroluminescent device as claimed in claim 14, wherein the first charge carrier injecting layer forms a type II semiconductor interface with the light emissive layer.

16. An electroluminescent device as claimed in any of claims 1 to 14, wherein the first charge carrier injecting layer is an anode electrode layer.

17. An electroluminescent device as claimed in any of claims 14 to 16, wherein the anode electrode layer has a workfunction greater than 4.3 eV.

18. An electroluminescent device as claimed in any preceding claim, wherein the second charge carrier injecting layer is a negative charge carrier transport layer which is located between the light emissive layer and a cathode electrode layer.

19. An electroluminescent device as claimed in claim 18, wherein the second charge carrier injecting layer forms a type II semiconductor interface with the light emissive layer.

20. An electroluminescent device as claimed in any of claims 1 to 17, wherein the second charge carrier injecting layer is a cathode electrode layer.

21. An electroluminescent device as claimed in any of claims 18 to 20, wherein the cathode electrode layer has a workfunction less than 3.5 eV.

22. An electroluminescent device as claimed in any of claims 14 to 21, wherein the electrode layer or at least one of the electrode layers is light transmissive.

23. An electroluminescent device comprising:

a first charge carrier injecting layer for injecting positive charge carriers;

a second charge carrier injecting layer for injecting negative charge carriers; and

a light emissive layer located between the charge carrier injecting layers and comprising a mixture of:

a first organic light emissive component for accepting and combining positive charge carriers from the first charge carrier injecting layer and negative charge carriers from the second light emissive component to generate light;

a second organic light emissive component for accepting and combining negative charge carriers from the second charge carrier injecting layer and positive charge carriers from the first light emissive component to generate light.

24. An electroluminescent device as claimed in claim 23, wherein the first component and the second component are at least partially phase-separated in the light emissive layer.

25. An electroluminescent device as claimed in claim 23 or 24, wherein the first component forms a type II semiconductor interface with the second component.

26. An electroluminescent device as claimed in any of claims 23 to 25, wherein the optical gaps of the first and second components are greater than 1.8 eV.

27. An electroluminescent device as claimed in any of claims 23 to 26, wherein the first component is F8.

28. An electroluminescent device as claimed in any of claims 23 to 27, wherein the second component is TFB.

29. An electroluminescent device as claimed in any of claims 23 to 28, wherein at least one of the first and second components is an organic material.

30. An electroluminescent device as claimed in any of claims 23 to 29, wherein at least one of the first and second components is a conjugated polymer material.

31. An electroluminescent device as claimed in any of claims 23 to 30, wherein the first charge carrier injecting layer is a positive charge carrier transport layer which is located between the light emissive layer and an anode electrode layer.

32. An electroluminescent device as claimed in any of claims 23 to 30, wherein the first charge carrier injecting layer is an anode electrode layer.

33. An electroluminescent device as claimed in claim 31 or 32, wherein the anode electrode layer has a workfunction greater than 4.3 eV.

34. An electroluminescent device as claimed in any of claims 23 to 33, wherein the second charge carrier injecting layer is a negative charge carrier transport layer which is located between the light emissive layer and a cathode electrode layer.

35. An electroluminescent device as claimed in any of claims 23 to 33, wherein the second charge carrier injecting layer is a cathode electrode layer.

36. An electroluminescent device as claimed in claim 34 or 35, wherein the cathode electrode layer has a workfunction less than 3.5 eV.

37. An electroluminescent device as claimed in any of claims 31 to 36, wherein the electrode layer or at least one of the electrode layers is light transmissive.

38. An electroluminescent device as claimed in any of claims 1 to 22 or 23 to 28, having a photoluminescence efficiency greater than 30%.

39. An electroluminescent device comprising:

- a first charge carrier injecting layer for injecting positive charge carriers;
- a second charge carrier injecting layer for injecting negative charge carriers;
- an organic light emissive layer located between the charge carrier injecting layers; and
- an organic charge transport layer located between the light emissive layer and one of the charge carrier injecting layers,

wherein the heterojunction formed between the transport layer and the light emissive layer is a luminescent type II heterojunction.

40. An electroluminescent device substantially as herein as described with reference to figures 3 to 21 of the accompanying drawings.

ABSTRACT**ELECTROLUMINESCENT DEVICES**

An electroluminescent device comprising: a first charge carrier injecting layer for injecting positive charge carriers; a second charge carrier injecting layer for injecting negative charge carriers; and a light emissive layer located between the charge carrier injecting layers and comprising a mixture of: a first component for accepting positive charge carriers from the first charge carrier injecting layer; a second component for accepting negative charge carriers from the second charge carrier injecting layer; and a third, organic light emissive component for accepting and combining charge carriers from the first and second components to generate light.

Figure 12

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Fig. 1a

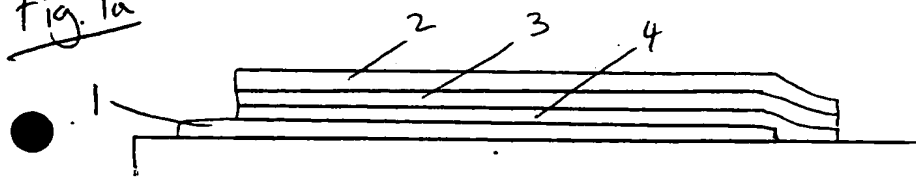


Fig. 1b

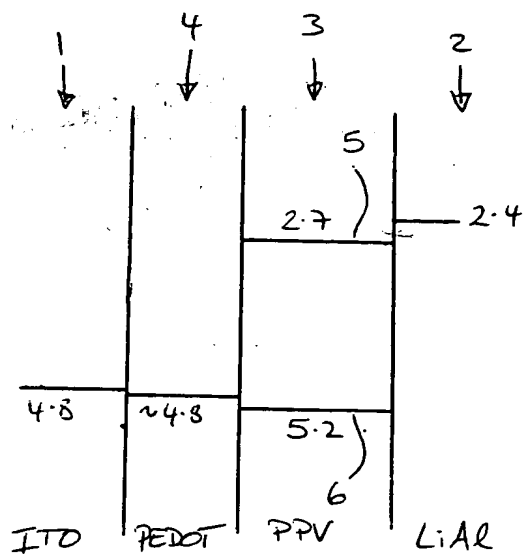
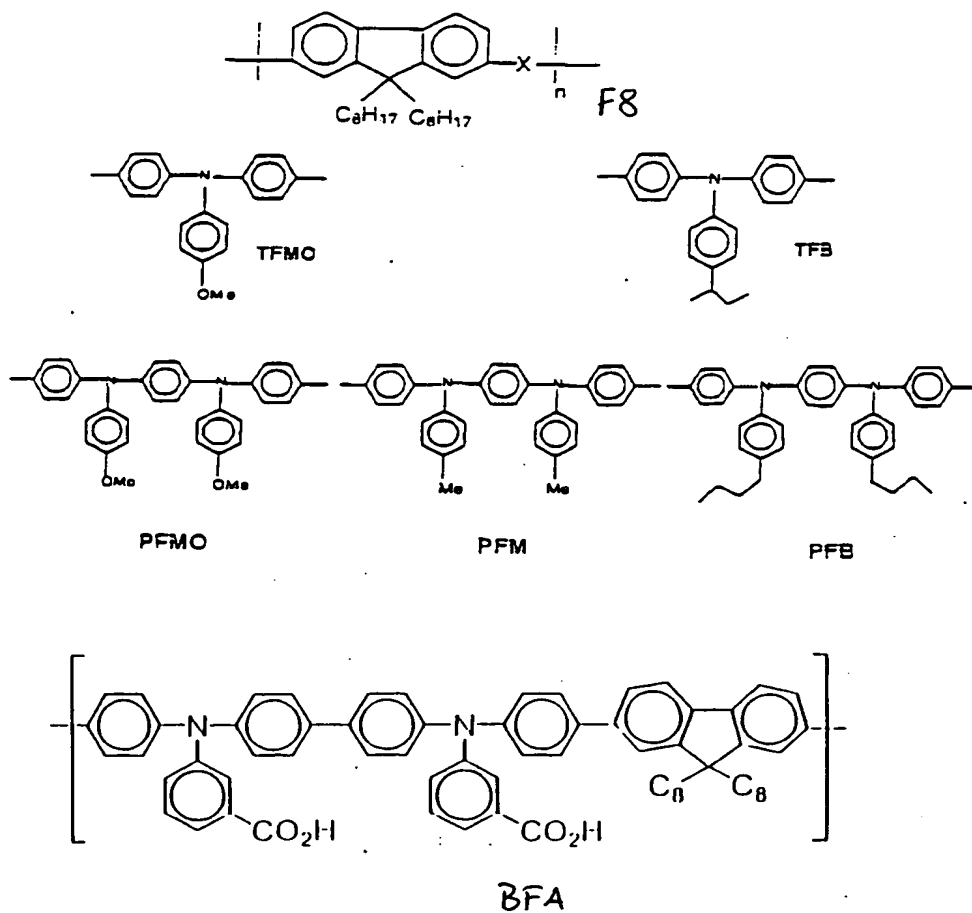


Fig. 3



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2/16

Fig. 2a

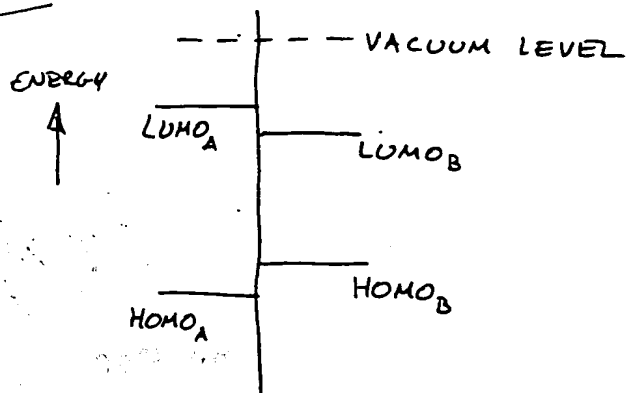
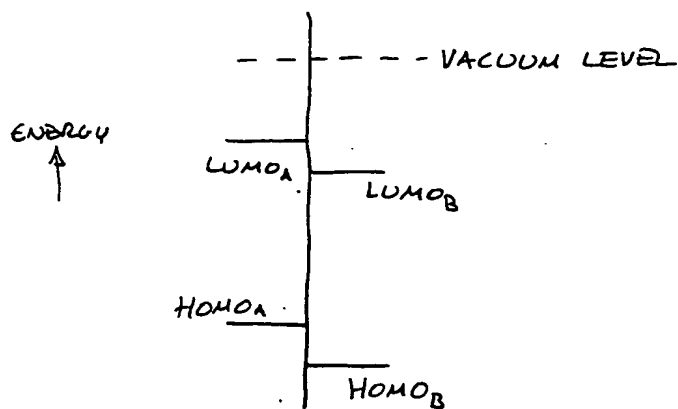


Fig. 2b



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3/16

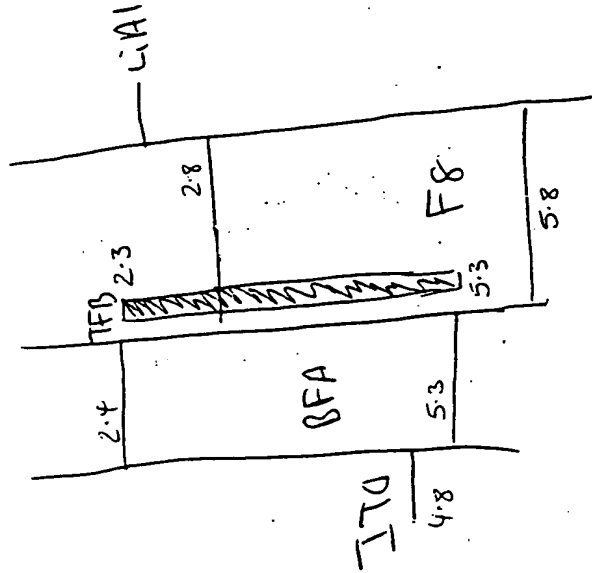


Fig. 9

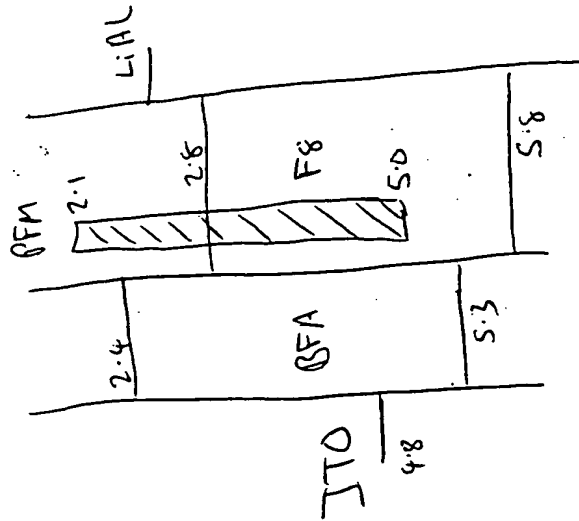


Fig. 6

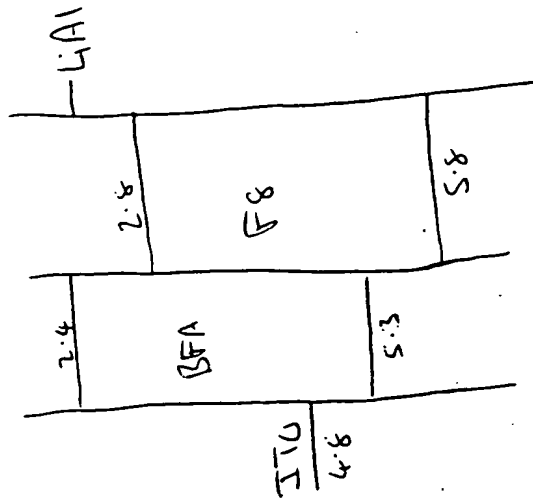


Fig. 4

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4/16

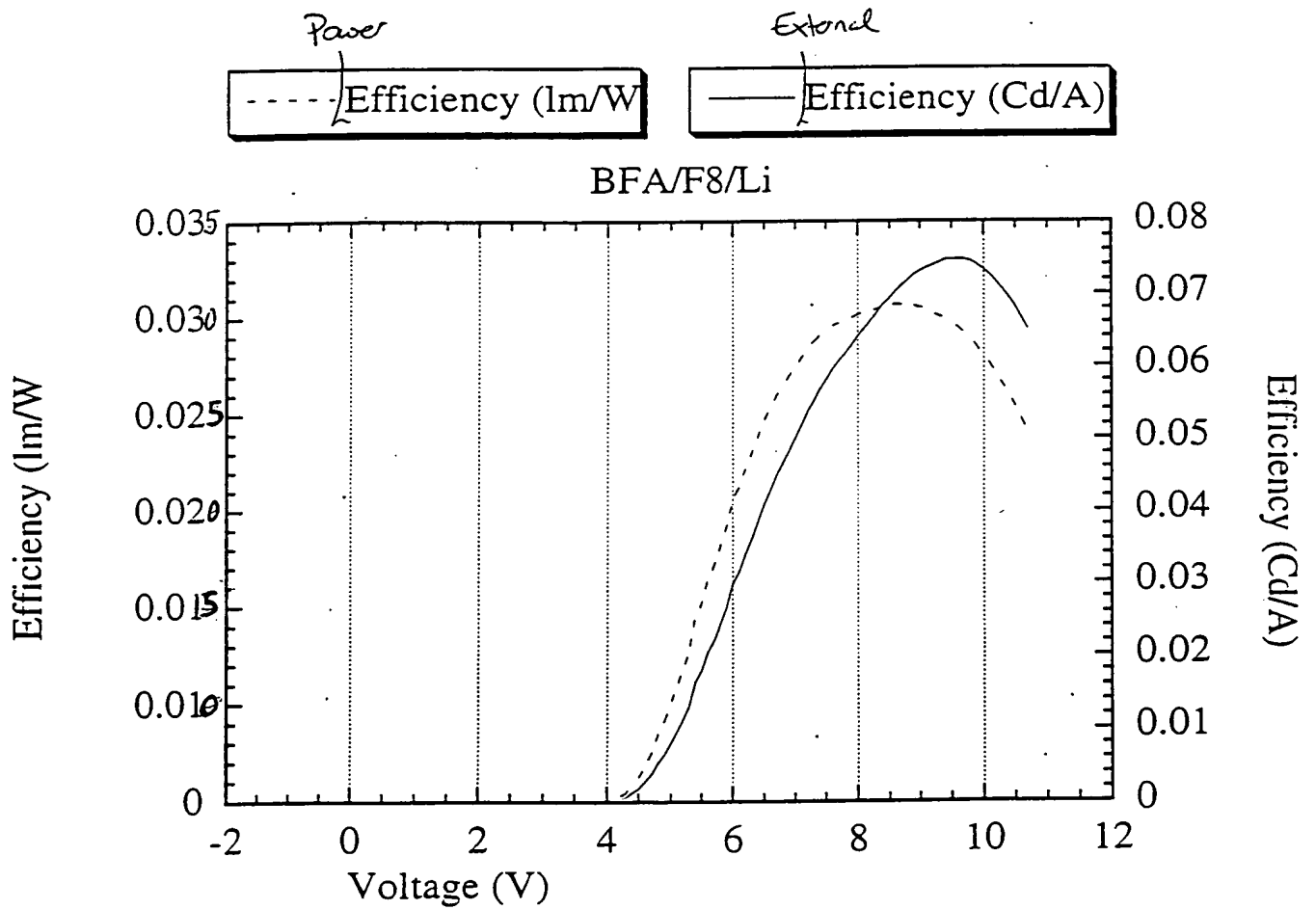


Fig. 5

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5/16

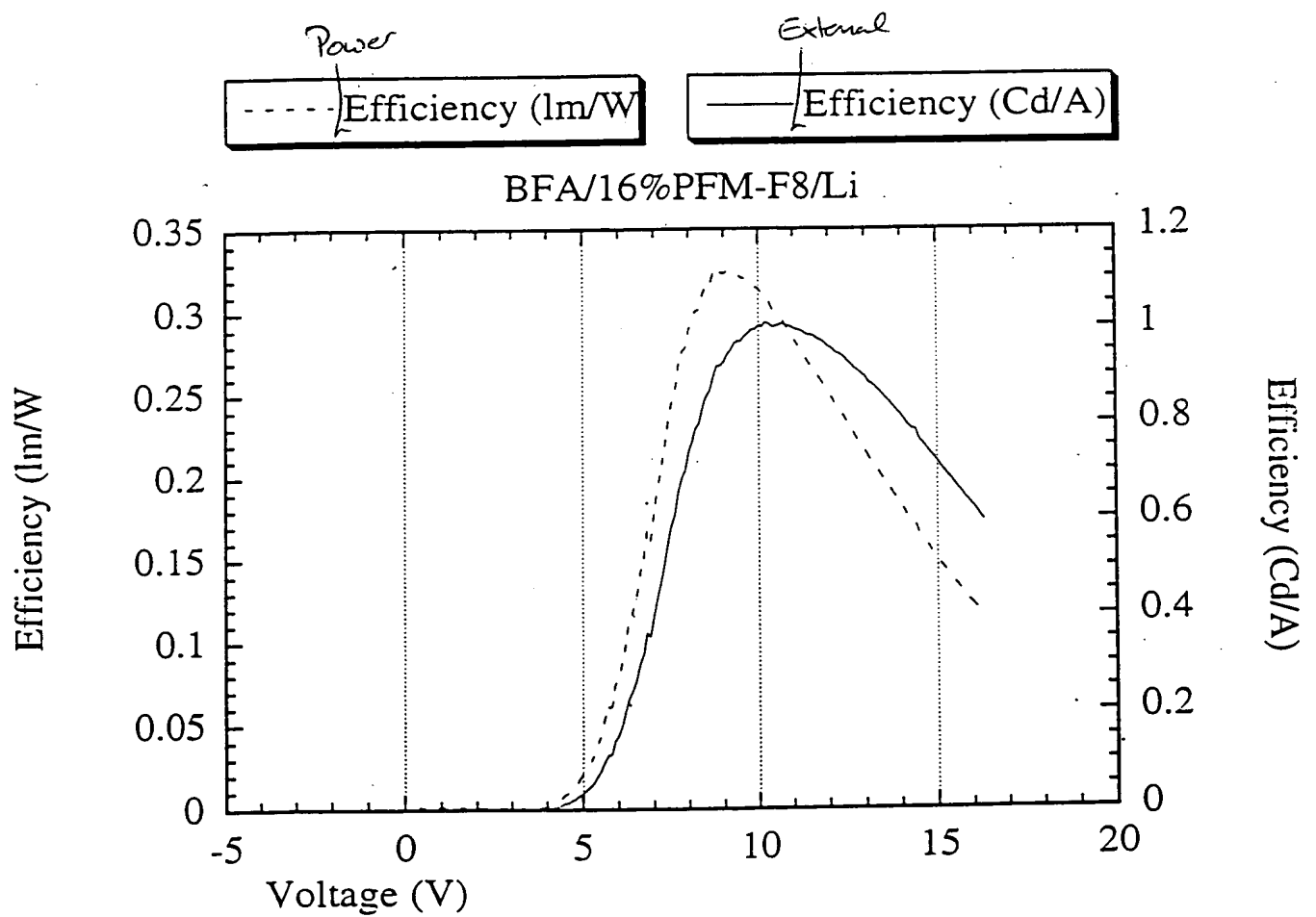


Fig. 7



6/16

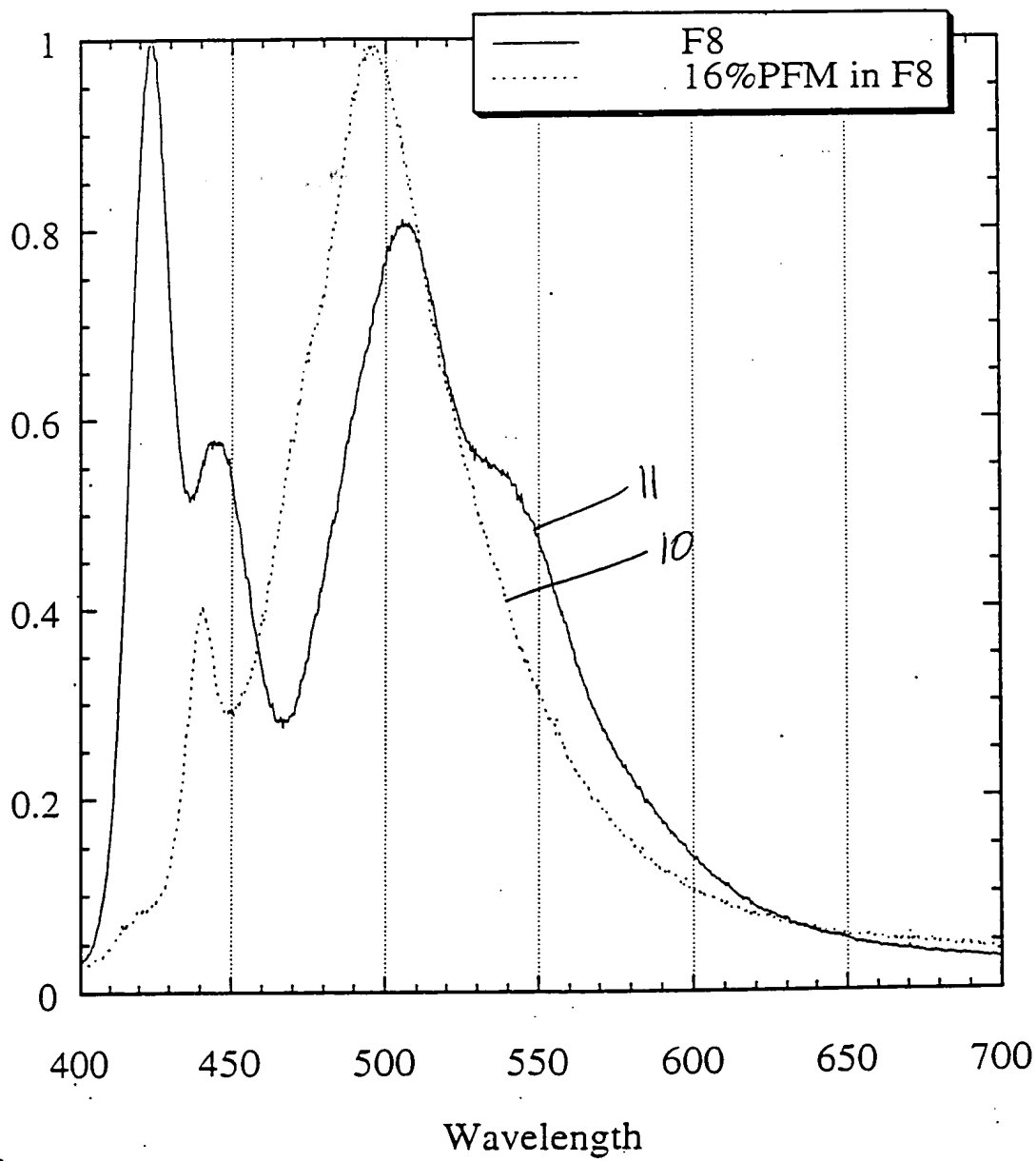


Fig. 8

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7/16

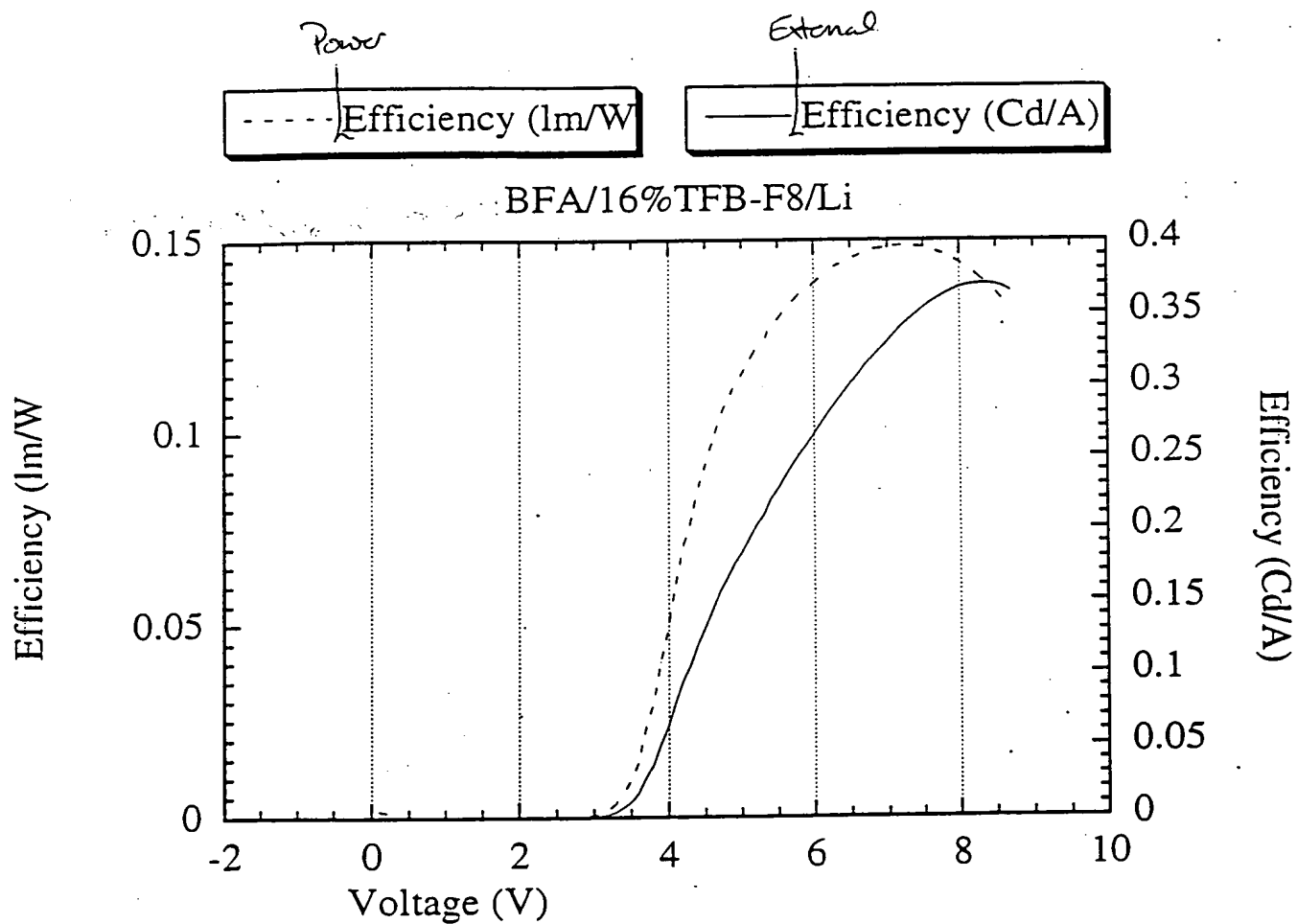


Fig. 10

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8/16

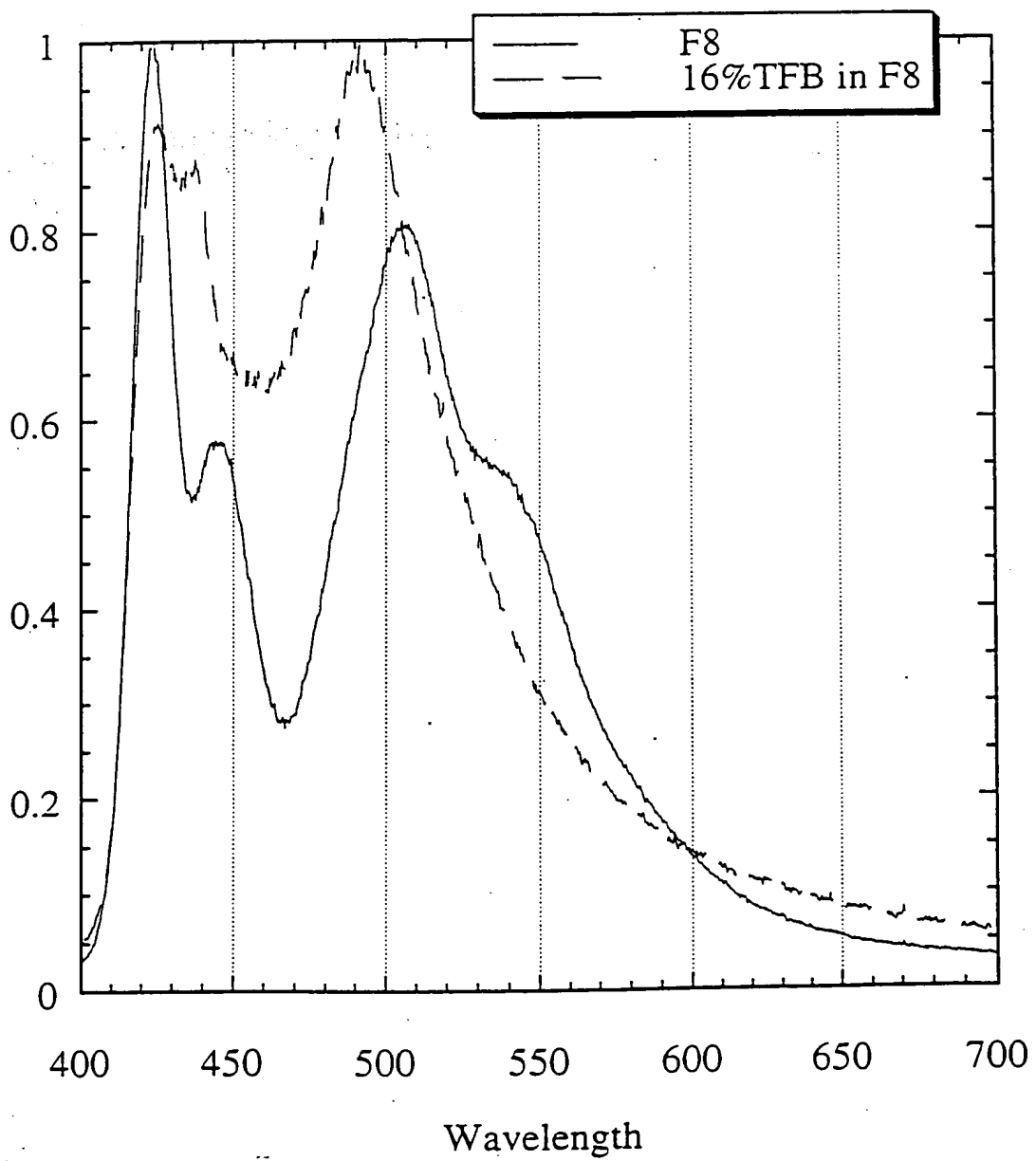


Fig 11

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9/16

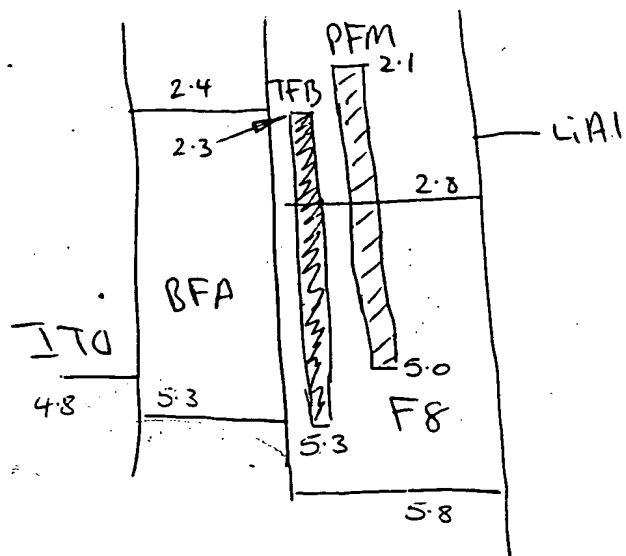


Fig. 12

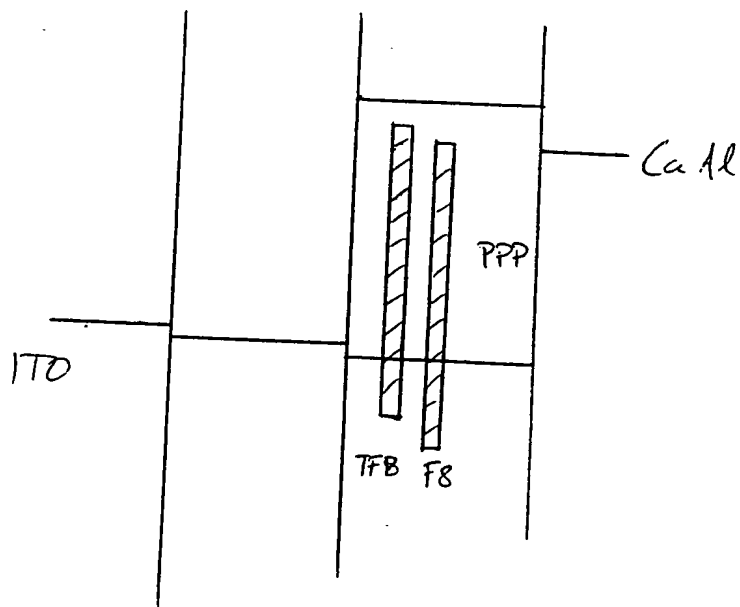


Fig. 21

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10/16

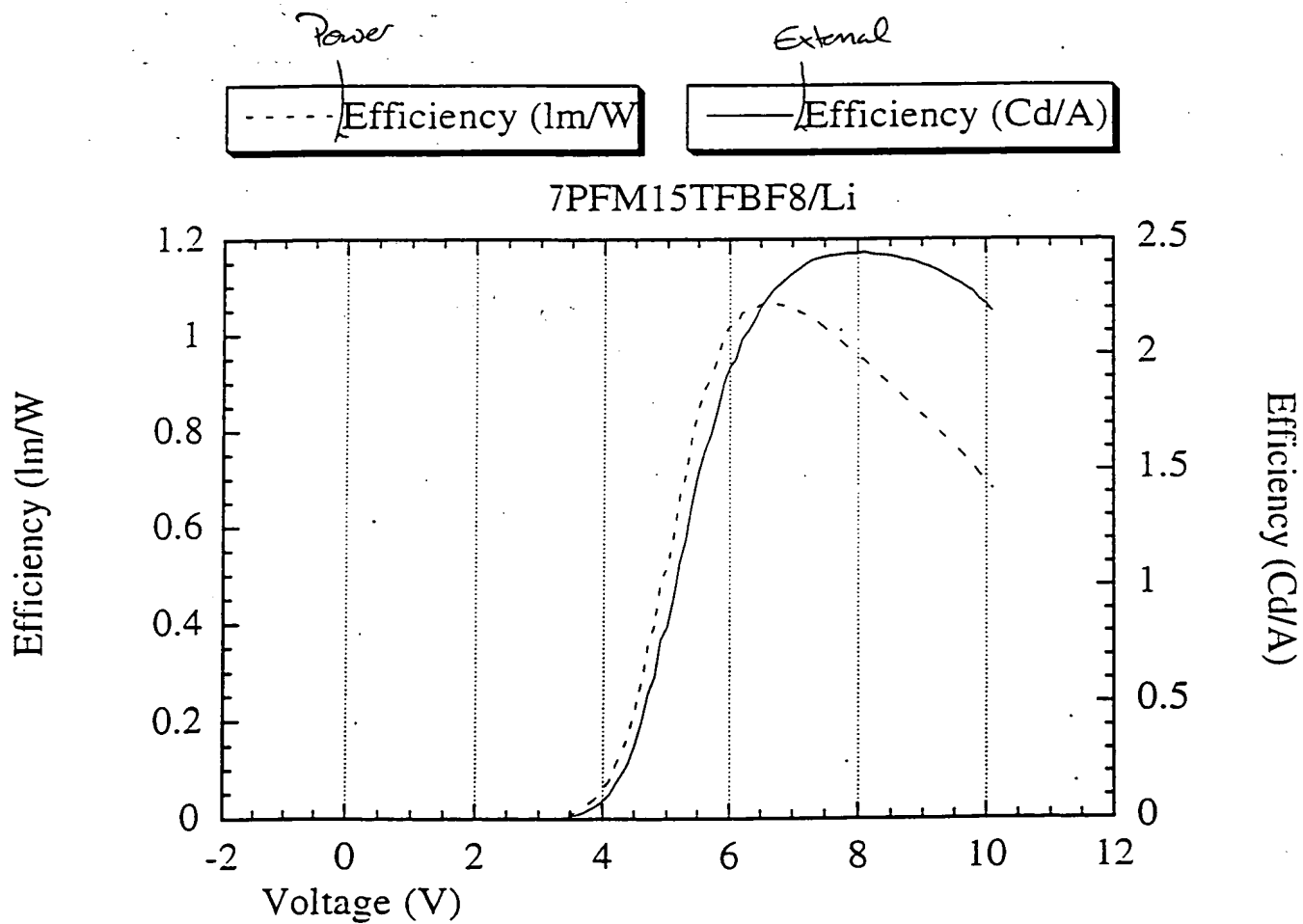


Fig. 13

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11/16

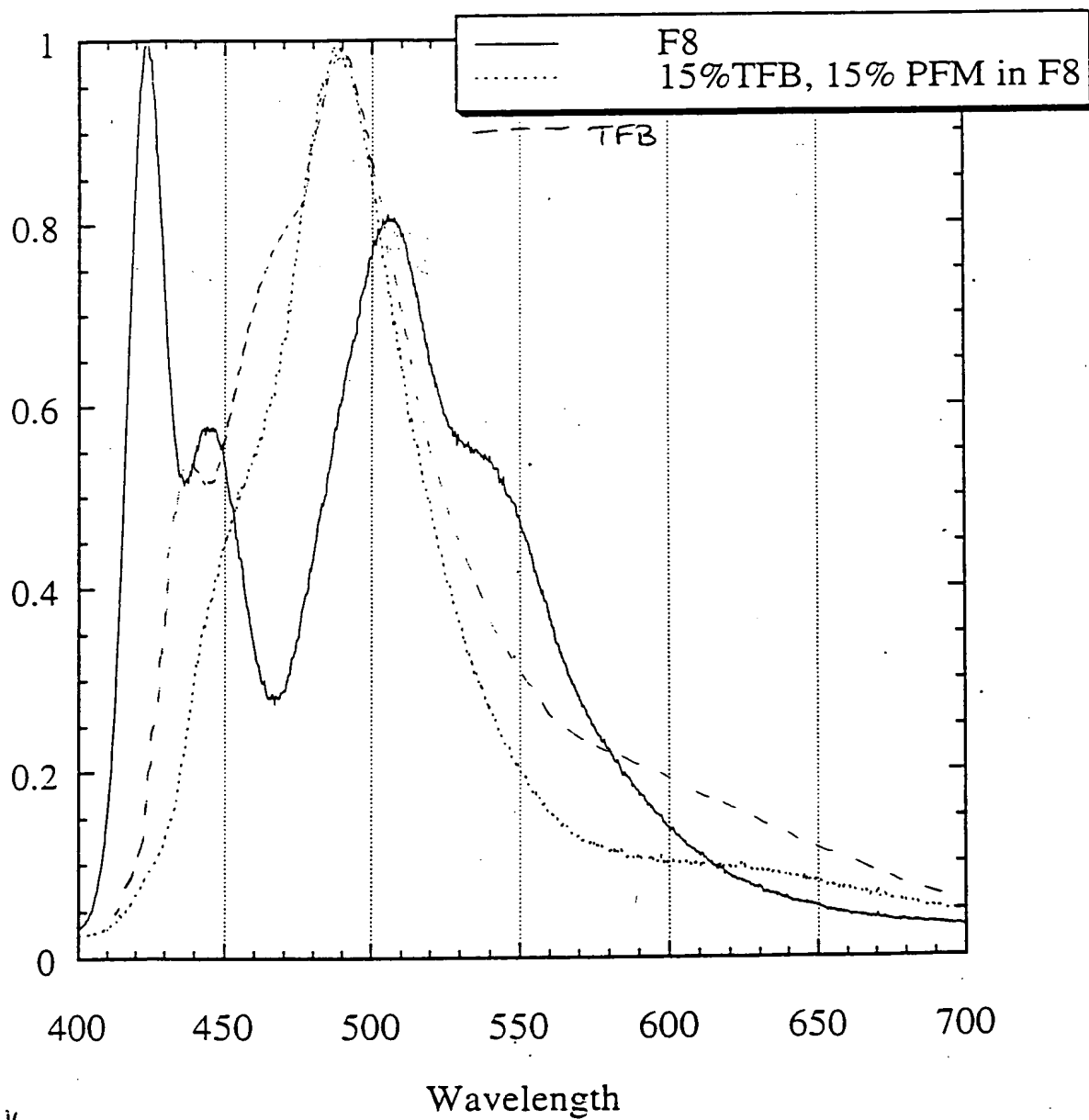


Fig. 14

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12/16

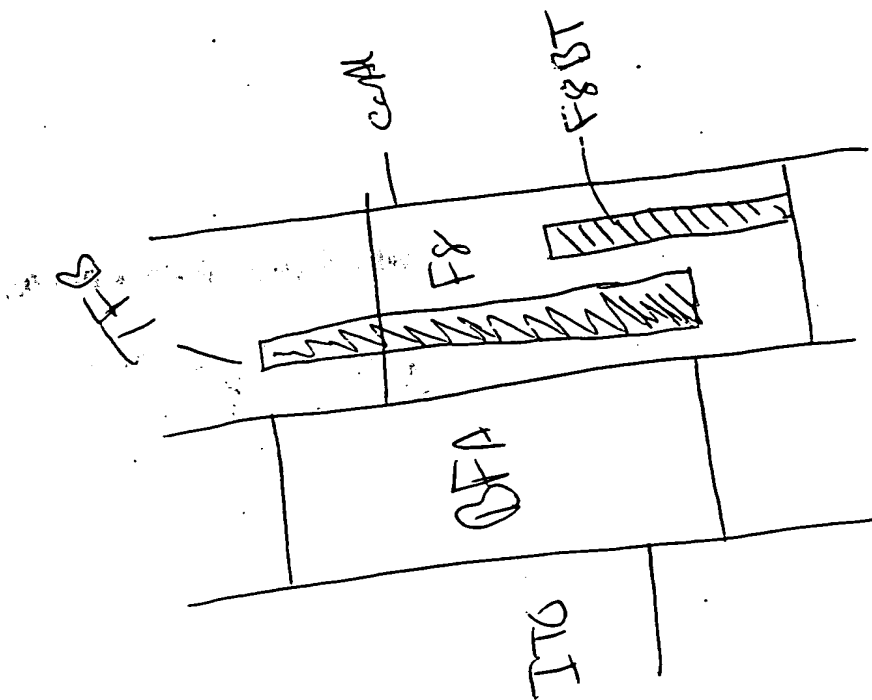


Fig. 18

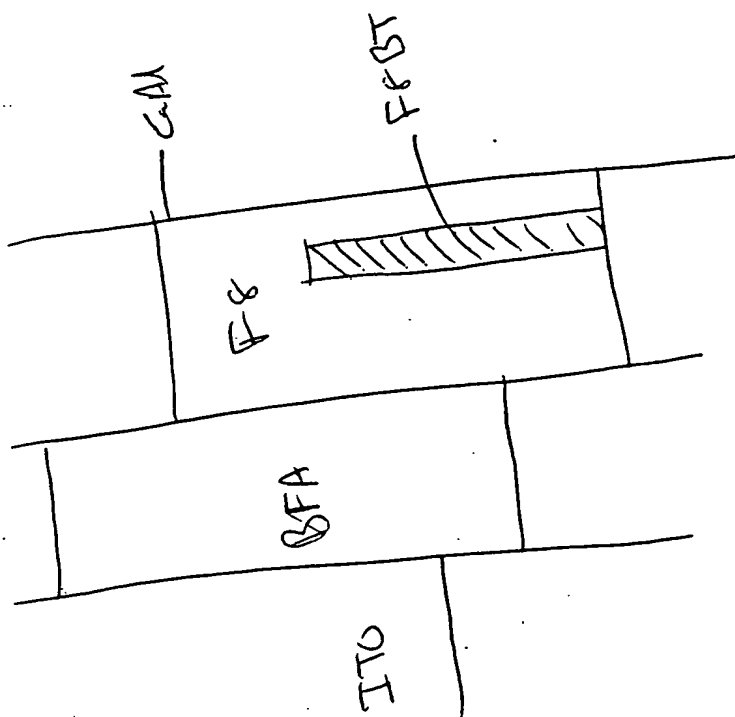


Fig. 15

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13/16

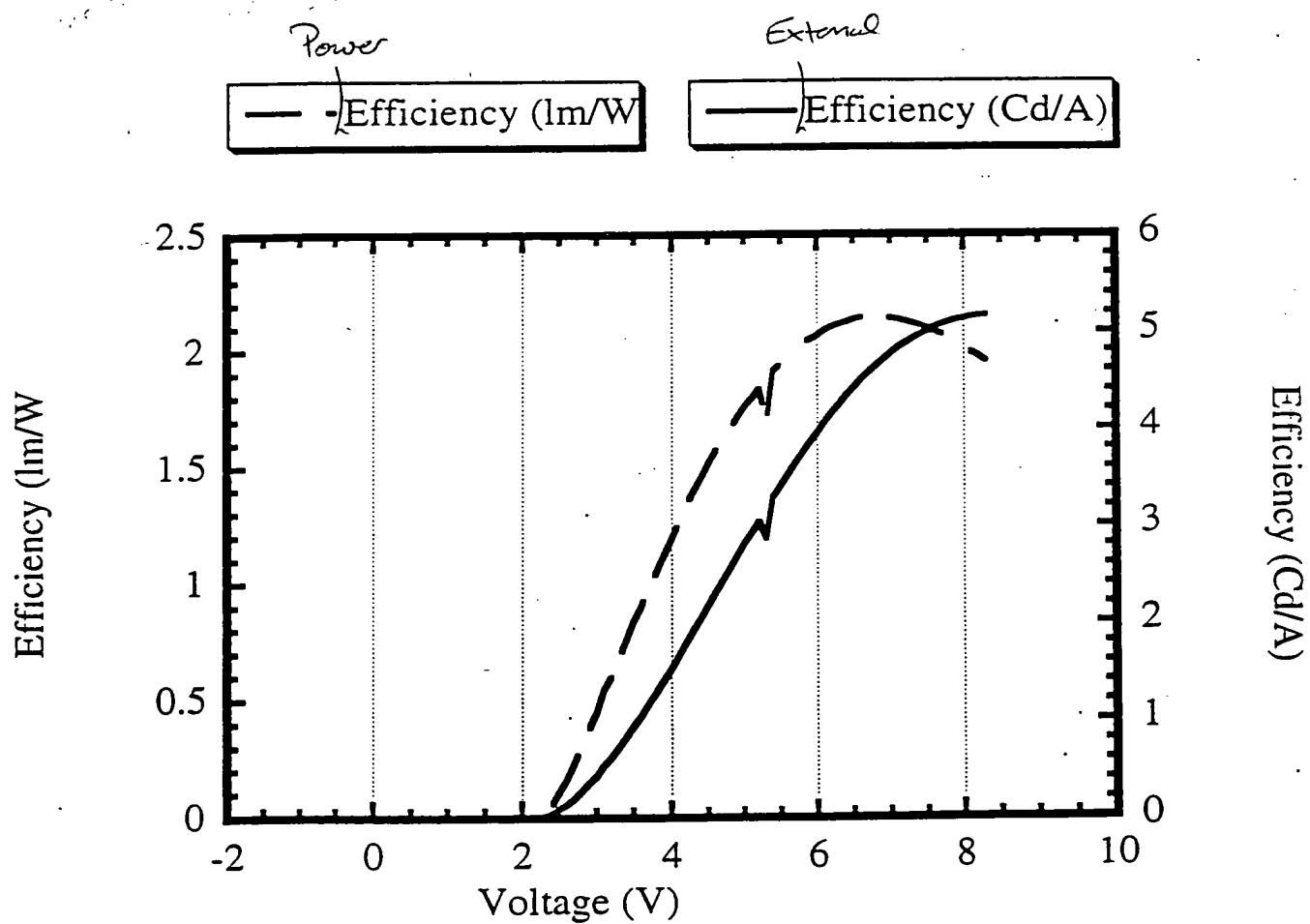


Fig. 16

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14/16

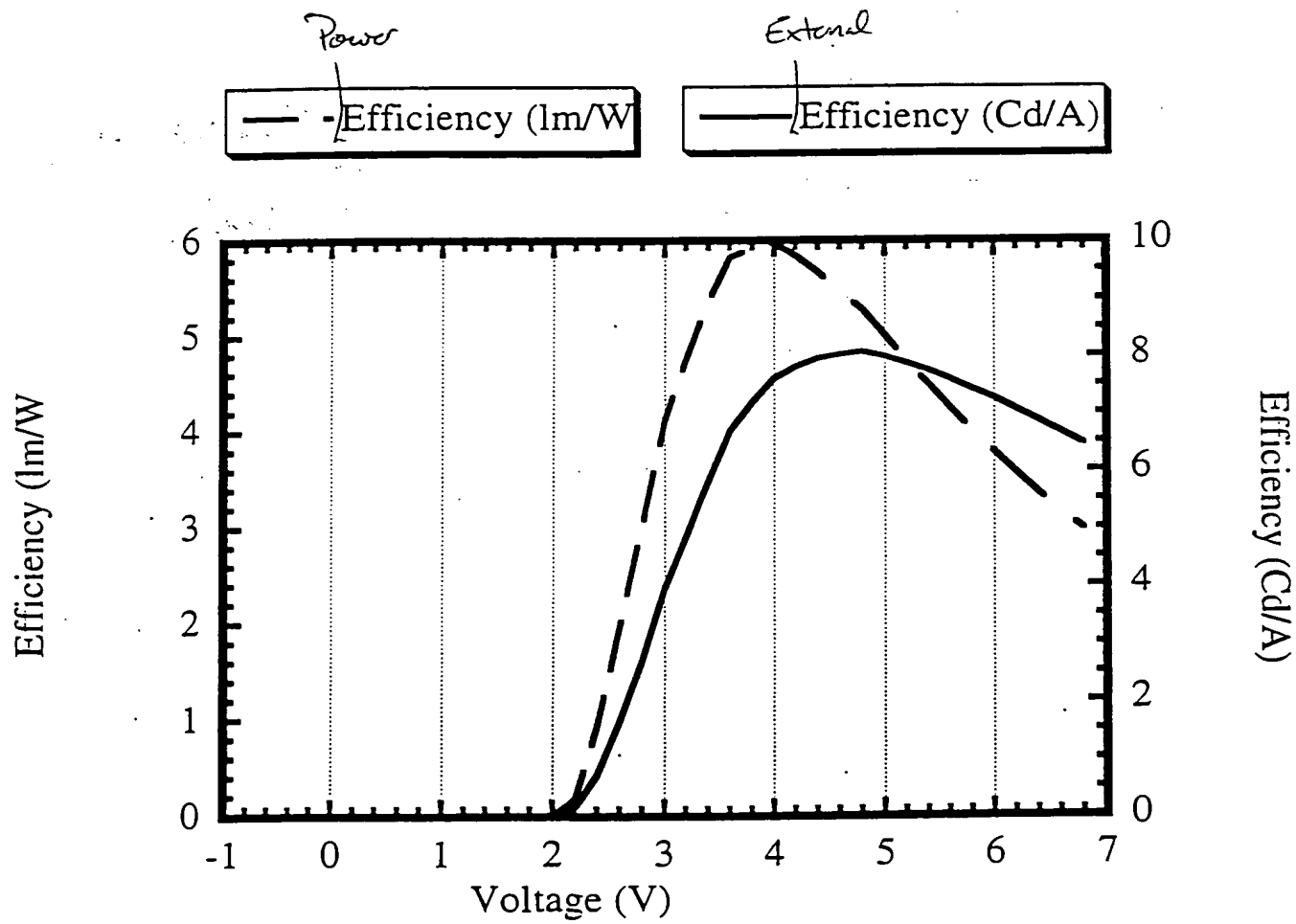


Fig. 17

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15/16

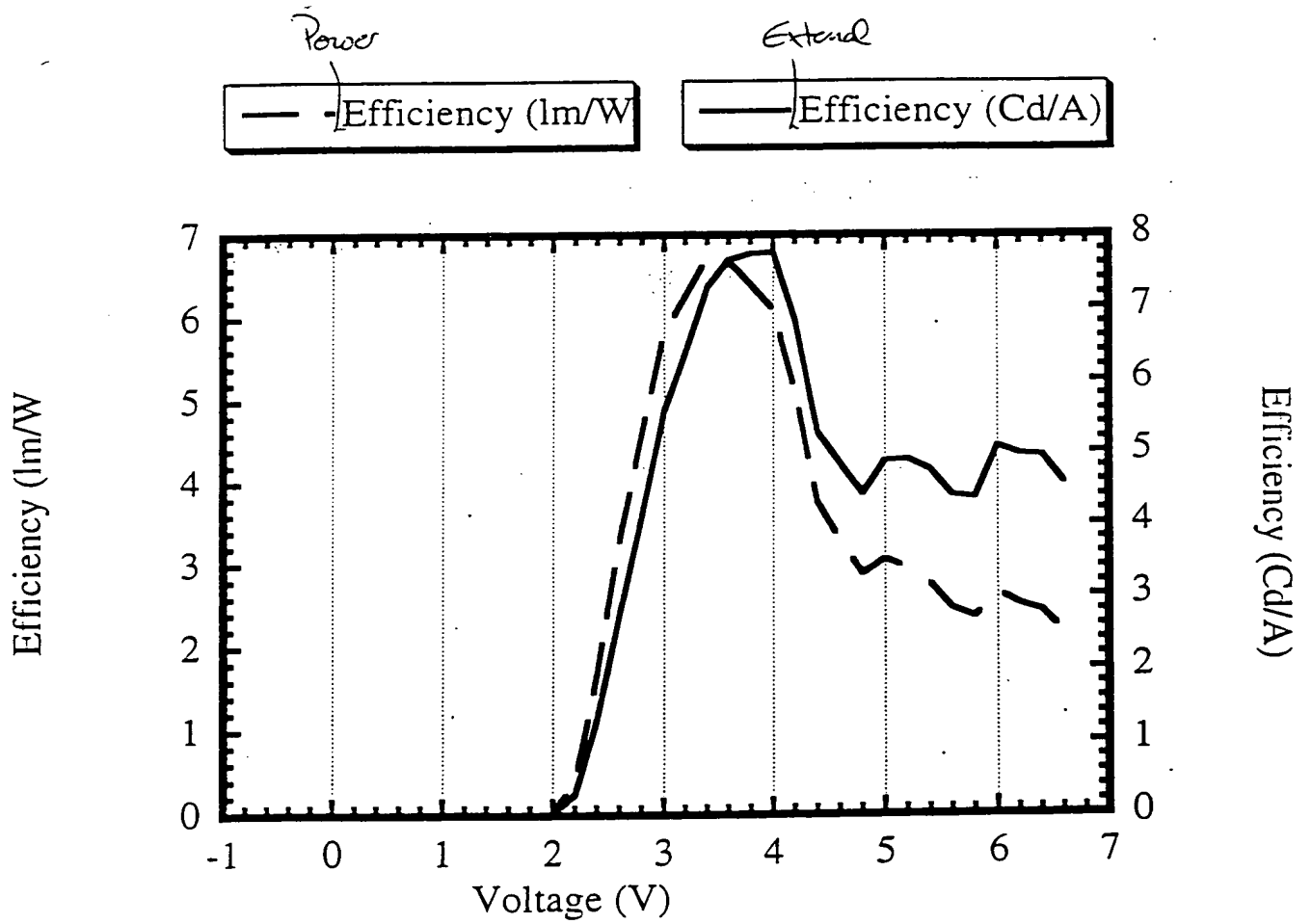


Fig. 19



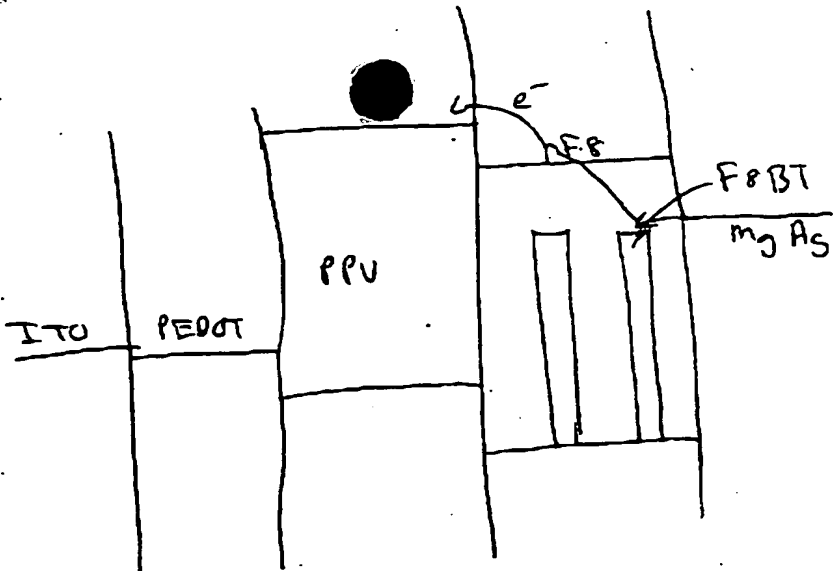


Figure 20.

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